

**Biodiesel and Renewable  
Diesel Emissions Study  
VOC, Carbonyl & N<sub>2</sub>O Emissions**

Christopher Brandow

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# Acknowledgements

MLD Southern Branch  
Organic Analysis

Richard Ong  
Michael Okafor  
Yong Yu  
Lyman Dinkins  
Christine Maddox  
Richard Ling  
Paul Rieger

# Engines and Fuels

Make/model/year	Emission Control Devices	Test fuels	Analyses
2000 Freightliner C15 Caterpillar		ULSD diesel, Soy-based biodiesel (S20, S50, S100), Animal-based ( A20, A50, A100), Renewable diesel (R20, R50, R100)	VOC Carbonyl N2O
2006 International ISM 370	EGR	ULSD diesel, Soy-based biodiesel (S20, S50, S100), Animal-based ( A20, A50, A100),	VOC Carbonyl
2008 Freightliner Mercedes Benz MBE 4000	DOC, DPF, EGR	ULSD diesel, Soy-based biodiesel (S20, S50, S100), Animal-based ( A20, A50, A100),	VOC Carbonyl

# Emissions Analyses

- Speciated non-methane hydrocarbons (NMHC)
- Carbonyl compounds
- Nitrous Oxide (N<sub>2</sub>O)

# Instrumentation

Analysis	Sample Container	Instrument
NMHC	Tedlar Bag	Gas Chromatograph (GC) with flame ionization detector (FID)
Carbonyls	DNPH* Cartridge	High performance liquid chromatograph (HPLC) with UV detector
N <sub>2</sub> O	Tedlar Bag	Fourier transform infrared spectrometer (FTIR)

\* Sampling cartridge impregnated with 2,4-dinitrophenylhydrazine

# Speciated Non-Methane Hydrocarbon Analysis

- Tedlar bag samples analyzed by 2 GC/FIDs, connected in parallel
  - *Light-end GC: C1 to C5 HCs*
  - *Mid-range GC: C6 to C12 HCs*
- Liquid nitrogen trapping of sample yields FID detection limits to very low ppbC

Dual Gas Chromatograph



H2 Generator

Mid-range GC

Light-end GC

# Speciated Non-Methane Hydrocarbon Analysis

- Compounds reported for this study:

*1,3-butadiene*

*benzene*

*toluene*

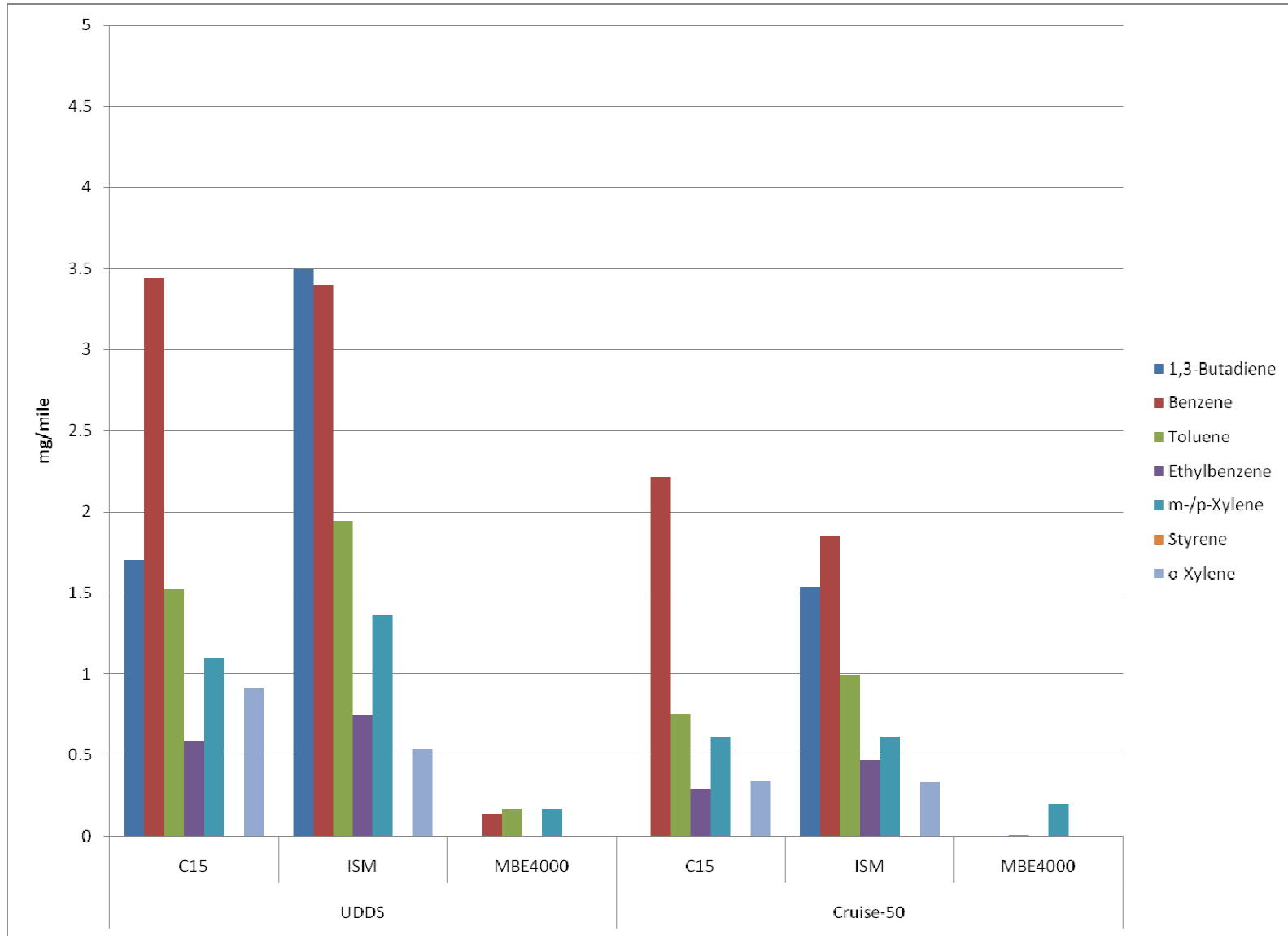
*ethylbenzene*

*m-/p-xylene*

*styrene*

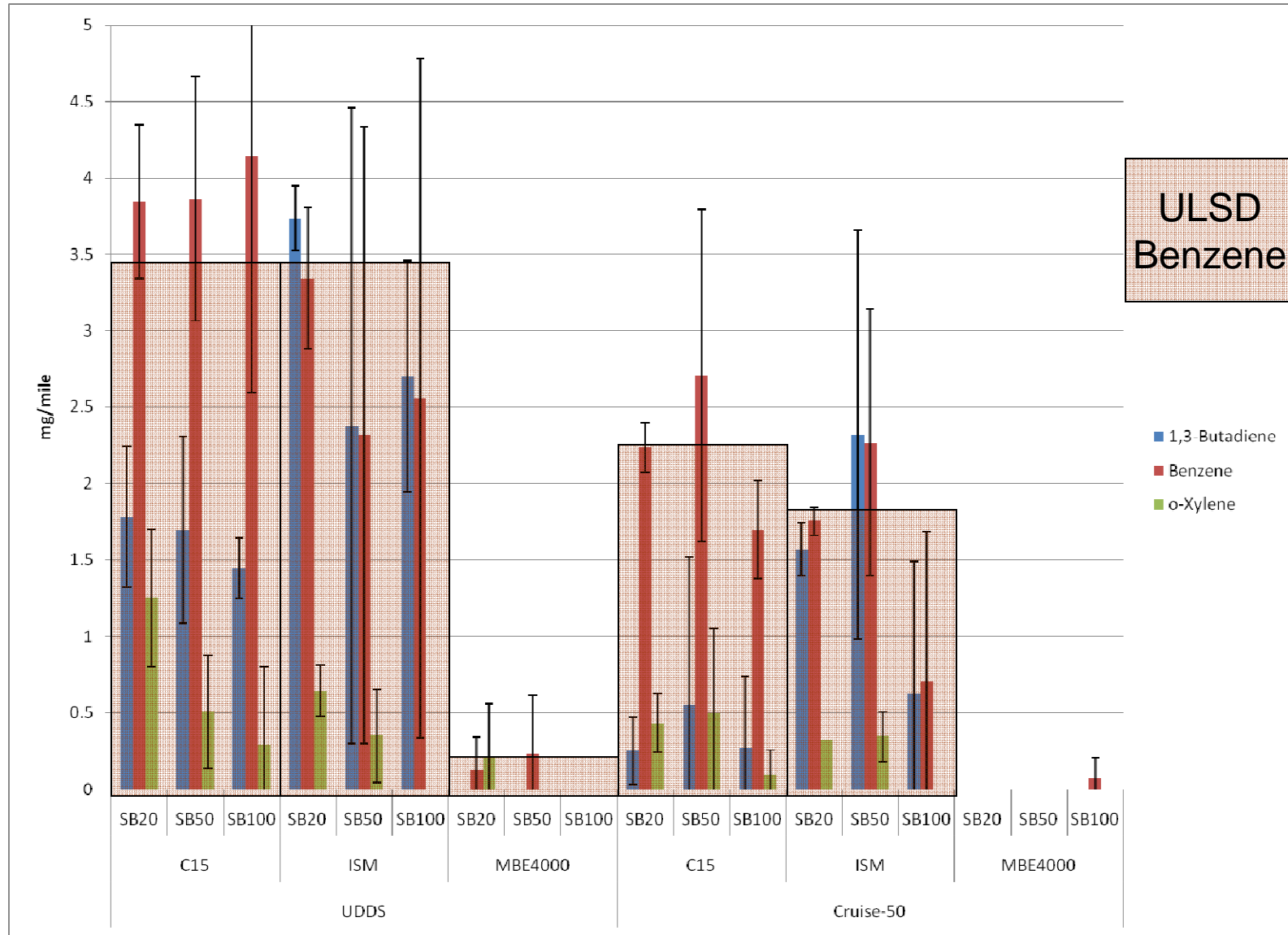
*o-xylene*

# Toxic VOC - ULSD

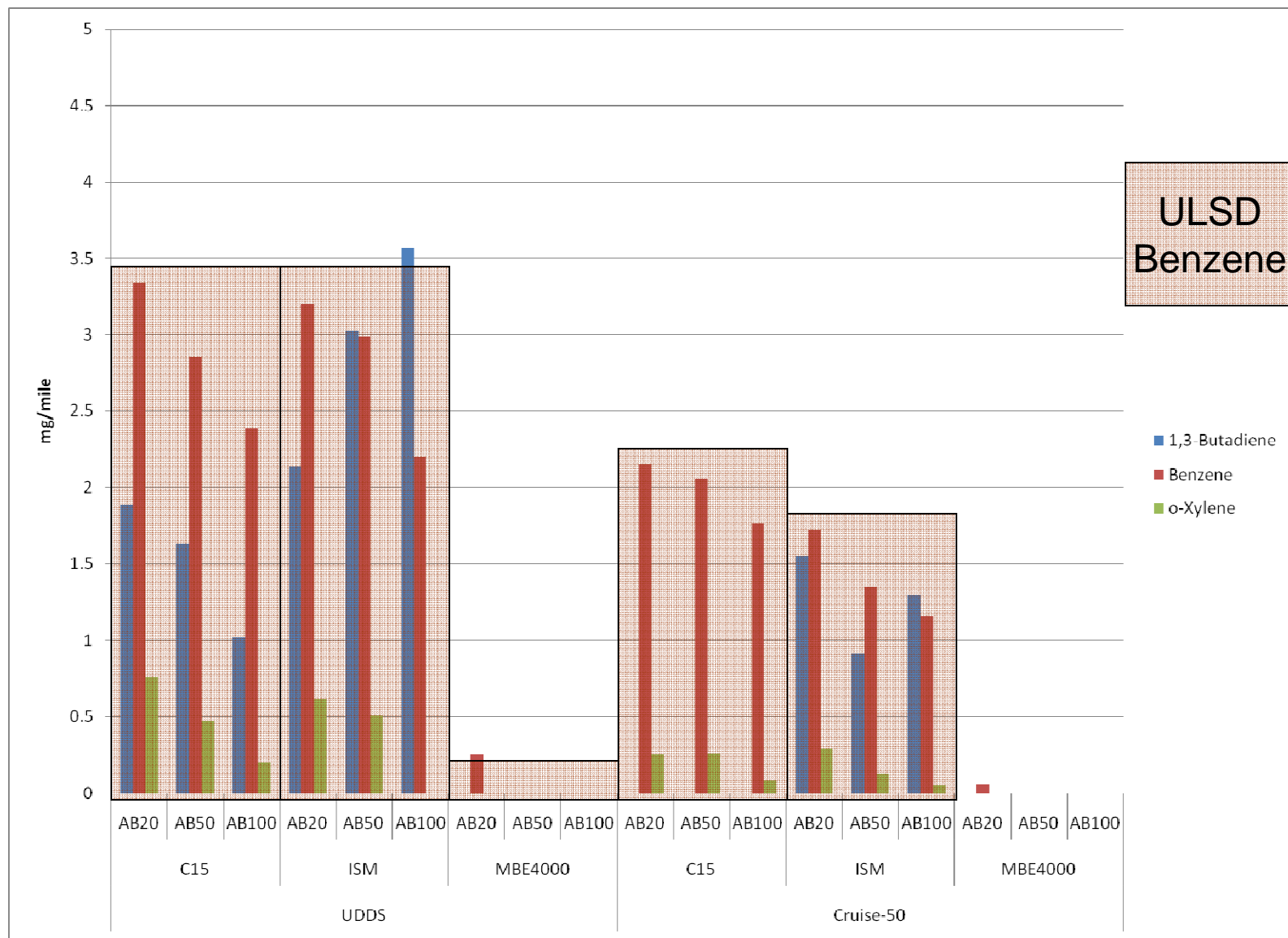




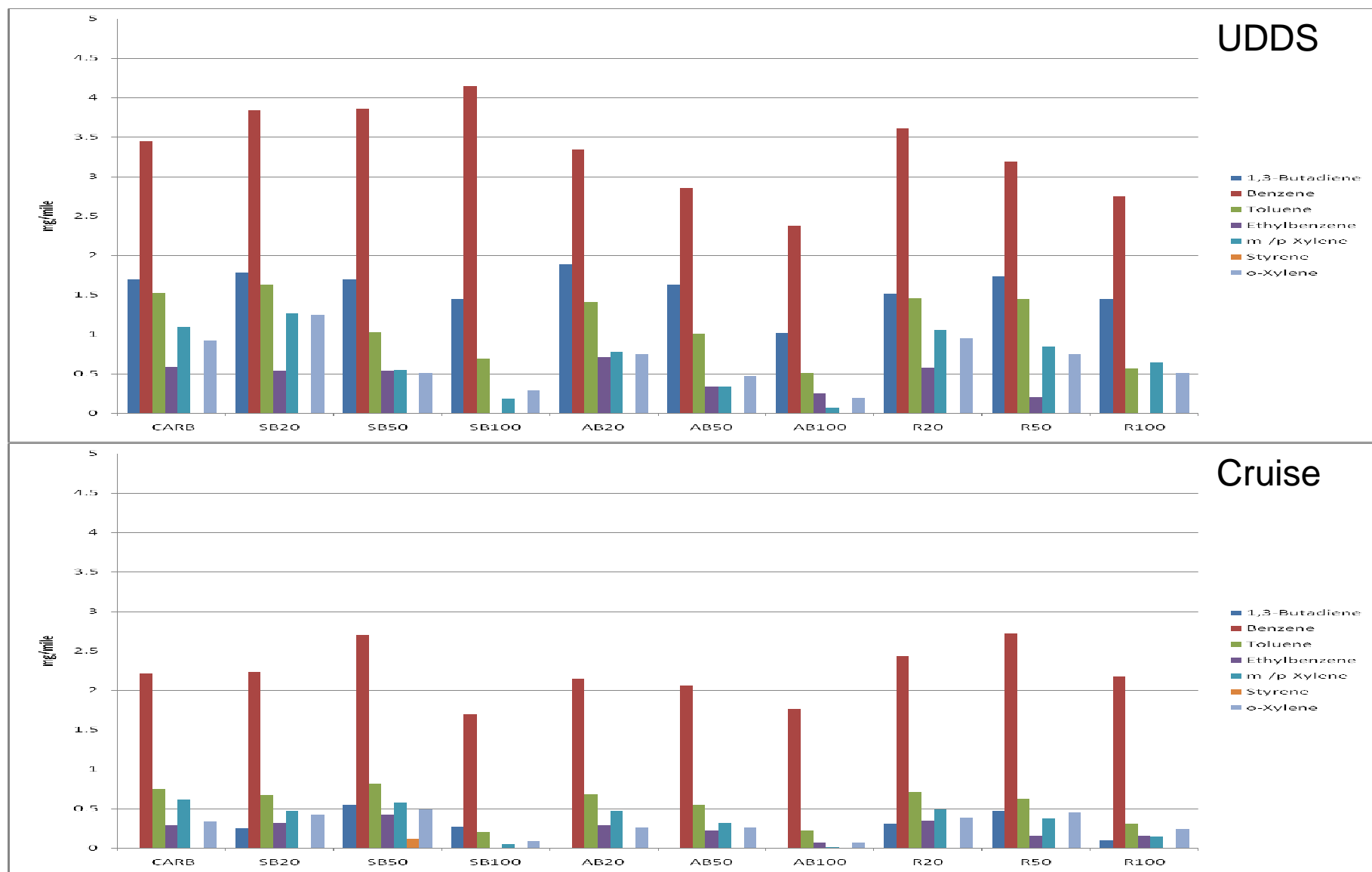
# Toxic VOC - Soy Biodiesel



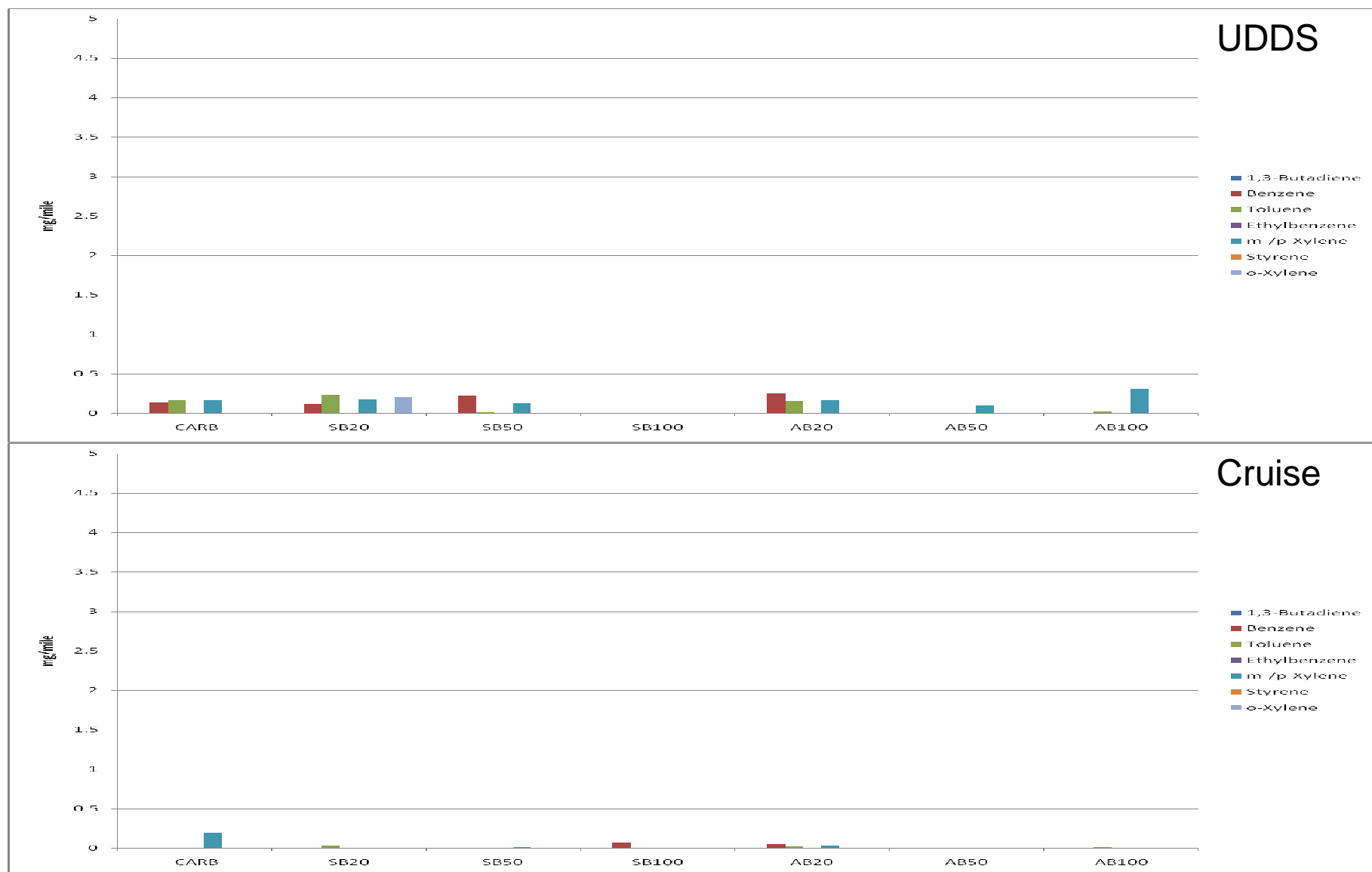
# Toxic VOC - Animal Biodiesel



# Toxic VOC -C15

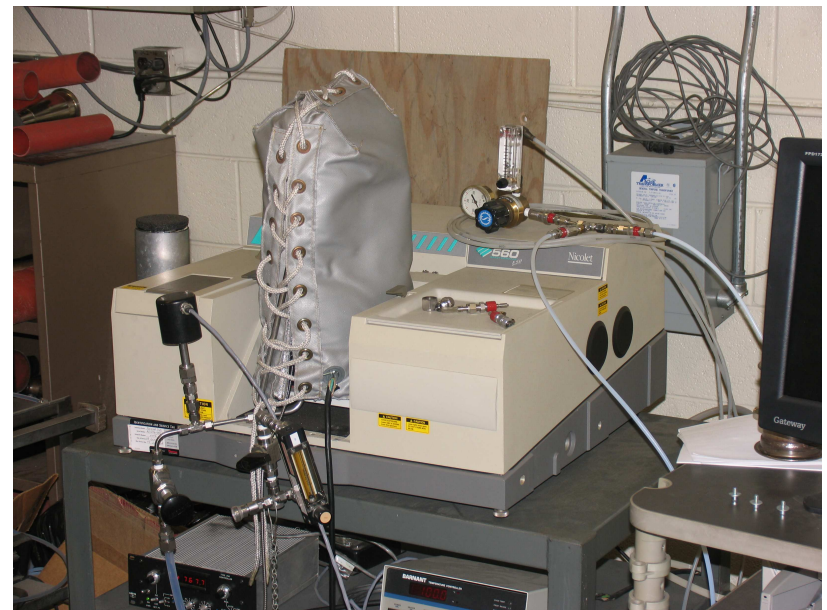


# Toxic VOC -MBE4000

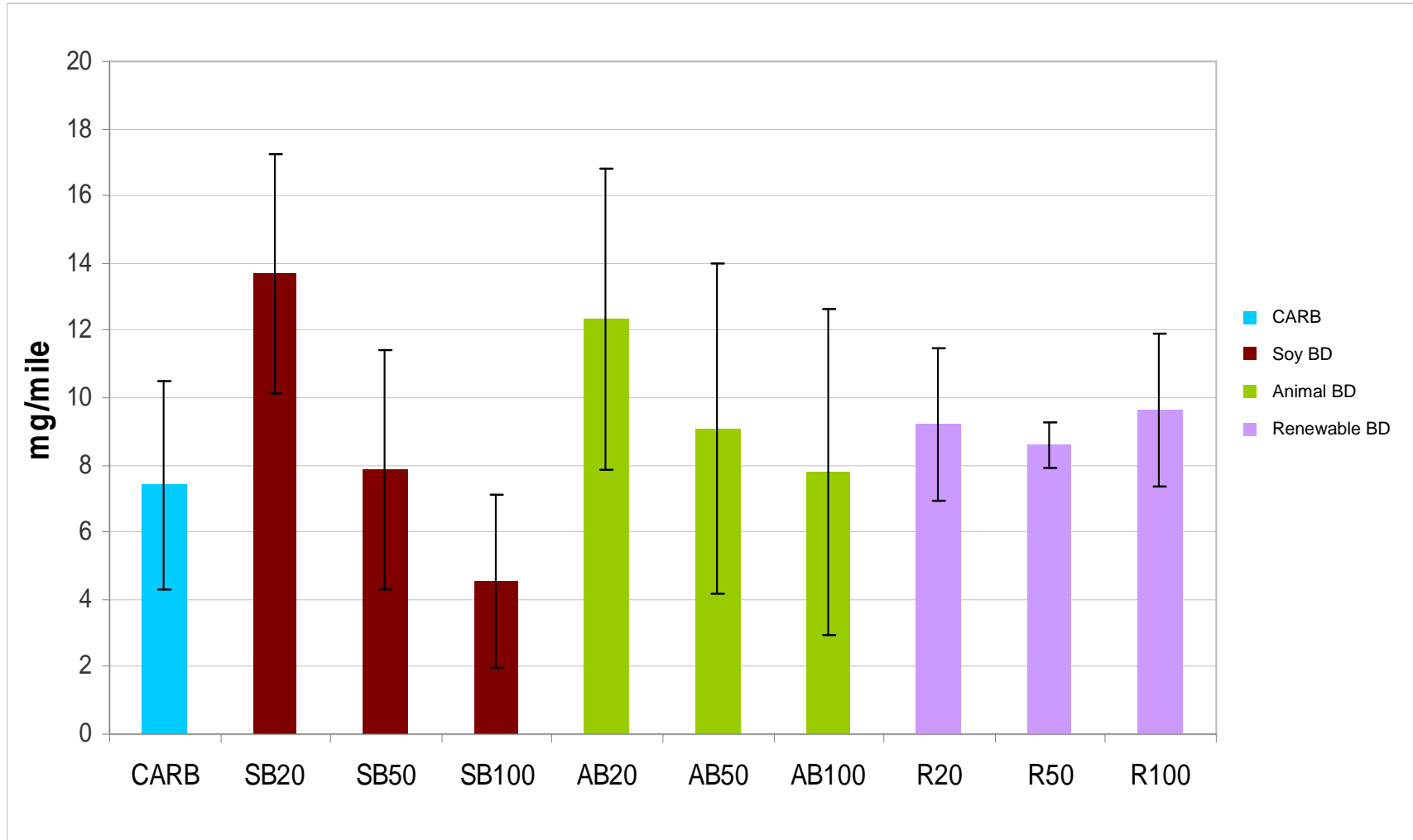


# NITROUS OXIDE ANALYSIS

- Tedlar bag samples analyzed by Fourier transform infrared spectroscopy (FTIR)
  - 10-Meter, folded path IR cell



# N<sub>2</sub>O – C15 Engine



# Carbonyl Analysis (Aldehydes and Ketones)

- Carbonyl group derivatized by DNPH in sampling cartridge\*
- Cartridges flushed with solvent to extract carbonyl compounds
- Solution analyzed by high performance liquid chromatograph (HPLC) with UV detection

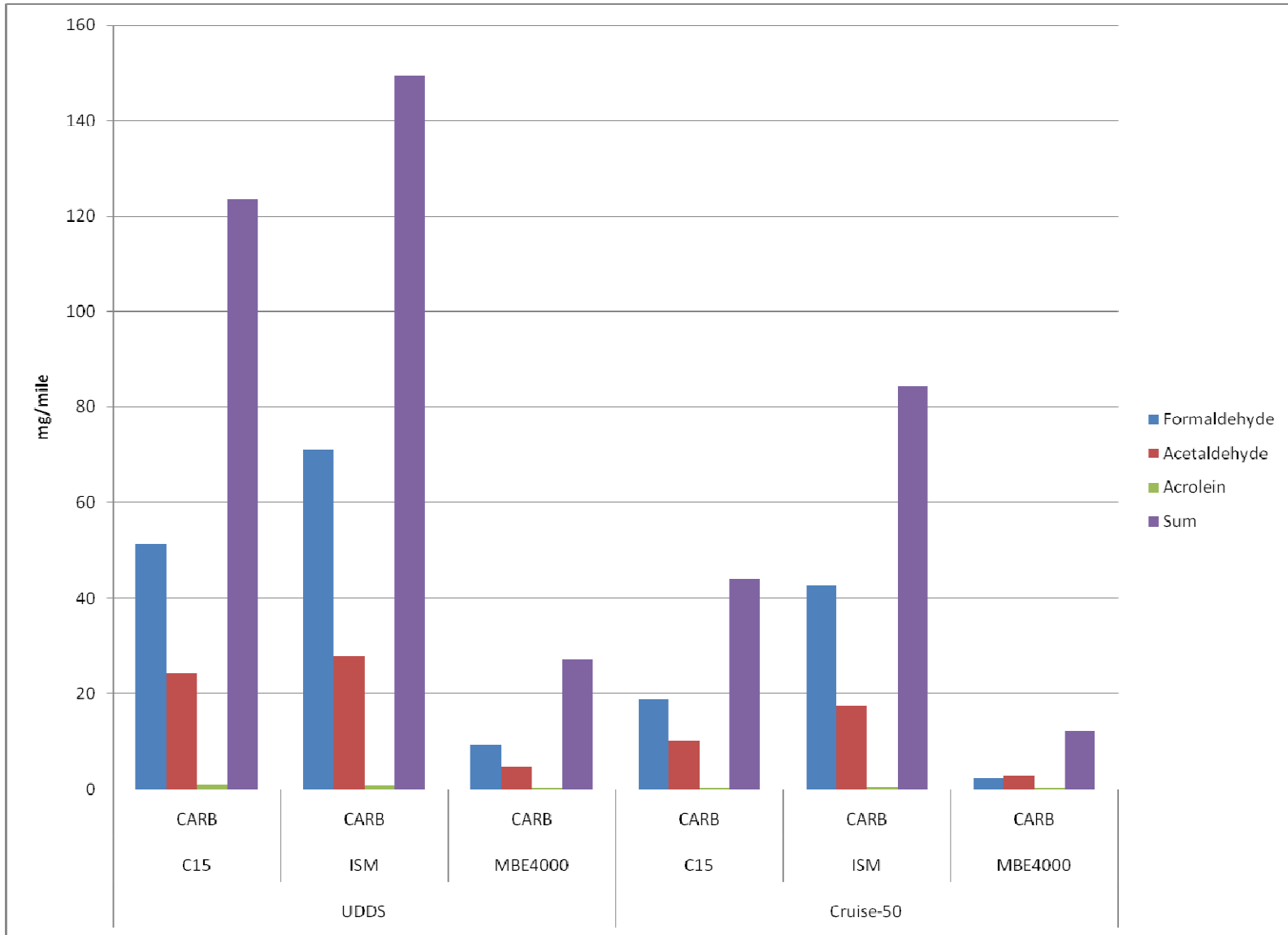


# Carbonyl Analysis (Aldehydes and Ketones)

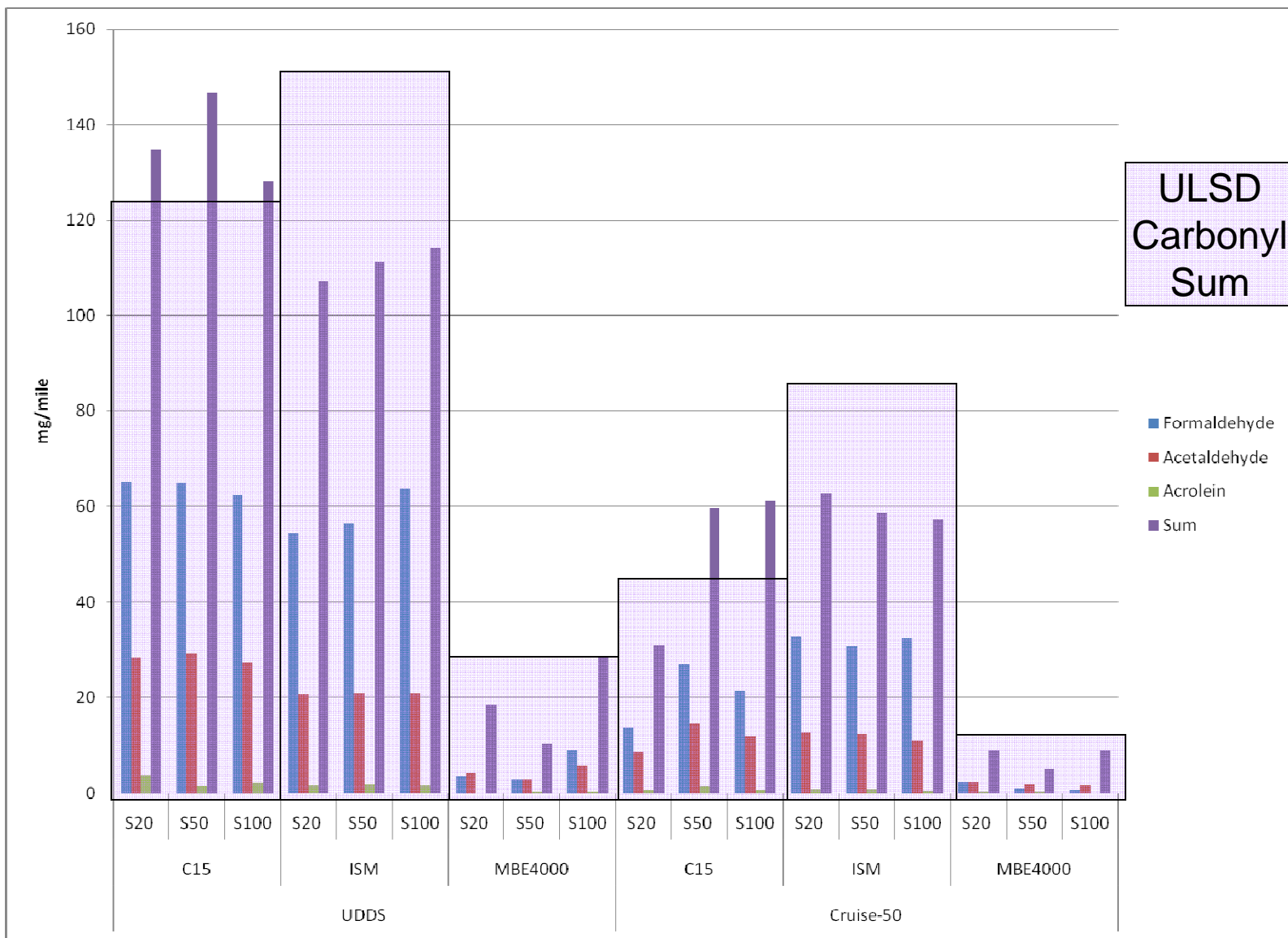
- This method measures:
  - formaldehyde
  - acetaldehyde
  - acrolein\*
  - 10 Other carbonyls (to C<sub>6</sub>)



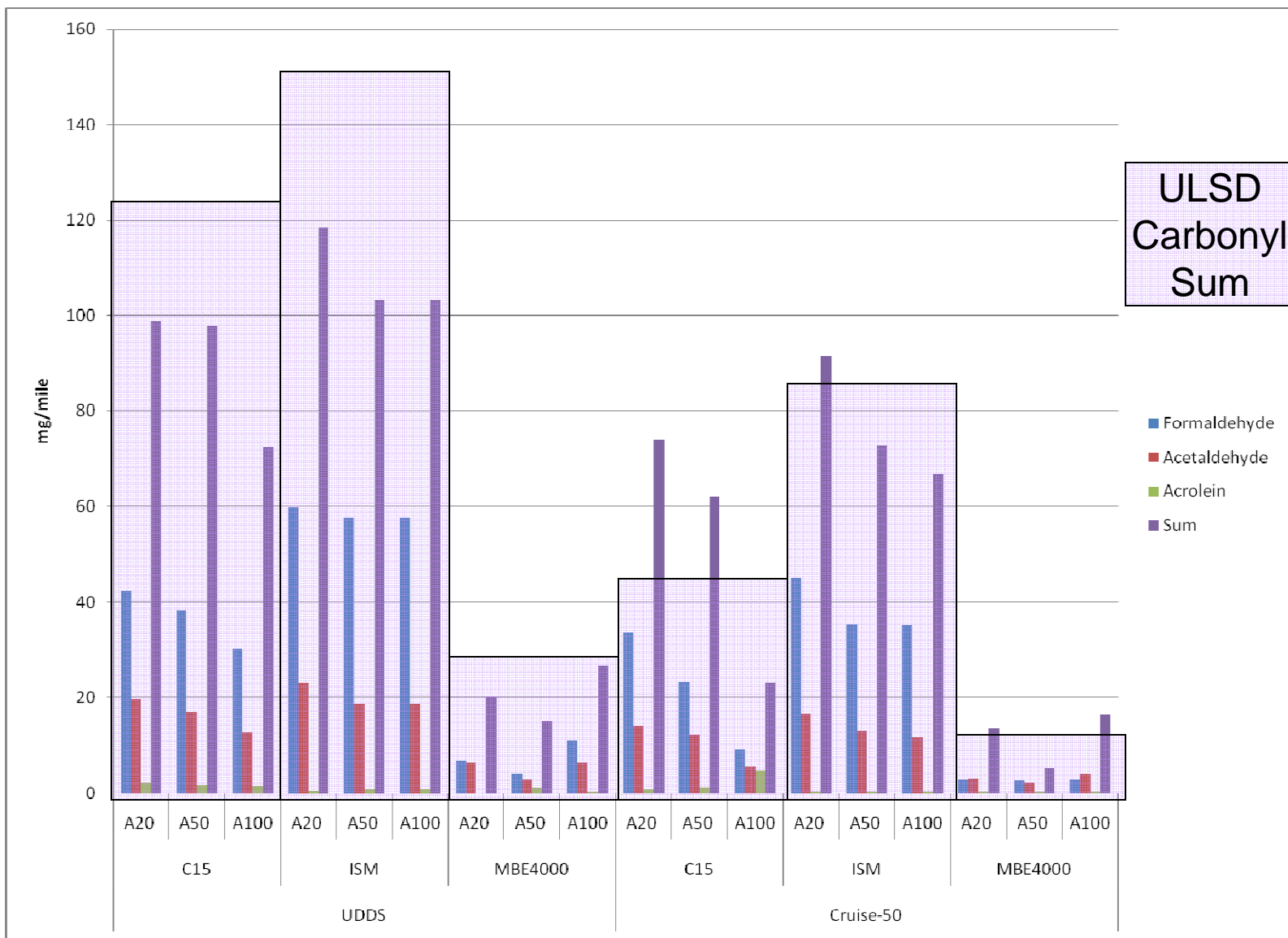
# Carbonyl - ULSD



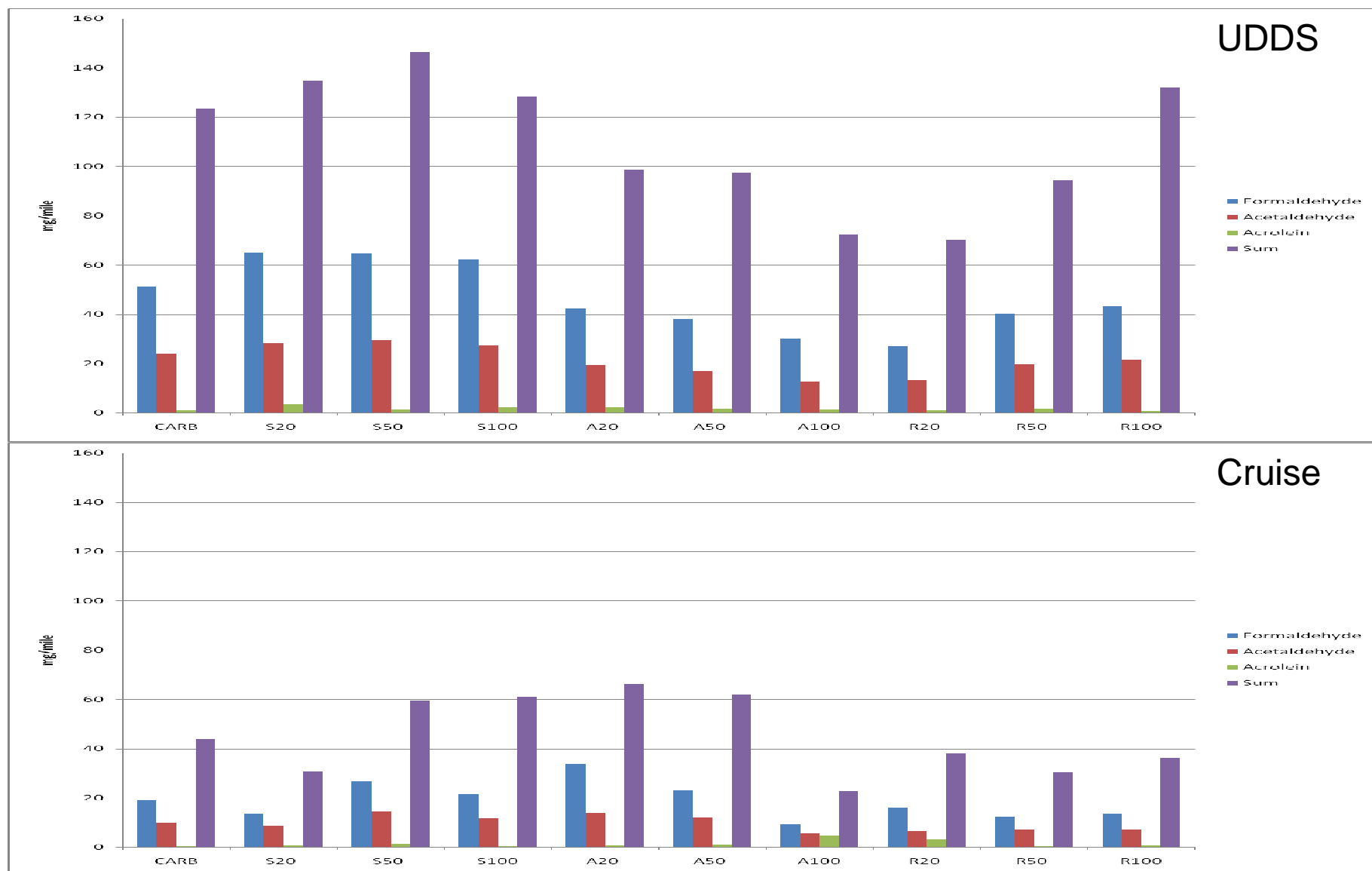
# Carbonyl - Soy Biodiesel



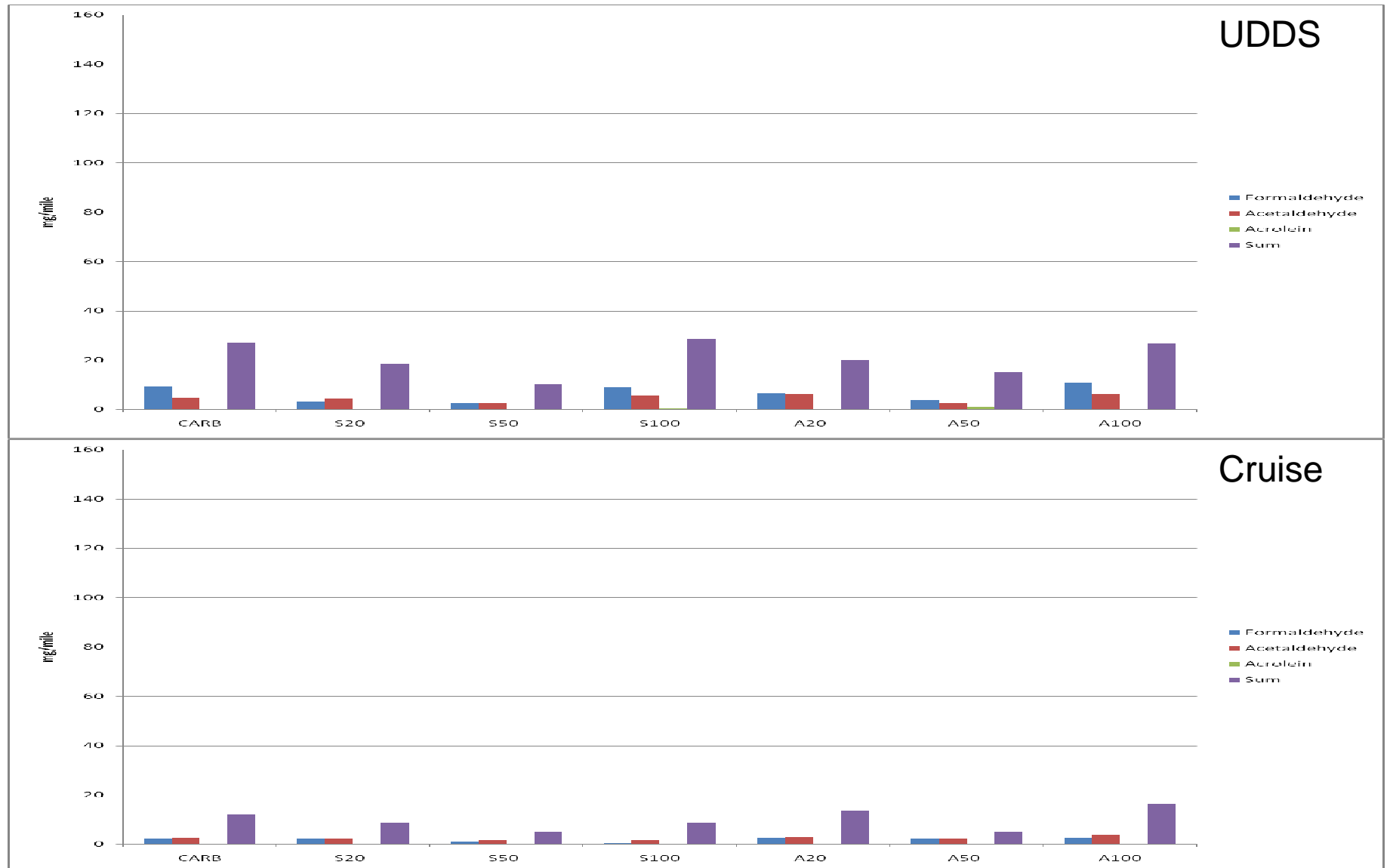
# Carbonyl - Animal Biodiesel



# Carbonyl-C15



# Carbonyl-MBE4000



# Summary - VOC

- Soy Biodiesel
  - No significant VOC increase versus ULSD Fuel
  - No trend with regard to increasing Biodiesel fractions
- Animal Biodiesel
  - Modest VOC decrease versus ULSD Fuel
  - VOC reduced with increasing Biodiesel fractions
- Renewable Biodiesel
  - Modest VOC decrease in UDDS cycle versus ULSD fuel but not in cruise
  - VOC reduced with increasing Biodiesel fraction in UDDS but not in cruise

# Summary – N<sub>2</sub>O

- No significant change in N<sub>2</sub>O emissions is observed for any fuel blend

# Summary - Carbonyl

- Soy Biodiesel
  - No significant changes versus ULSD Fuel
  - No trend with regards to increasing Biodiesel fractions
- Animal Biodiesel
  - Modest decrease versus USLD Fuel in UDDS Cycle only
  - emissions reduced with increasing Biodiesel fractions.
- Renewable Biodiesel
  - No significant changes versus ULSD



# Summary - Engines

- VOC
  - C15 and ISM engines perform similarly to each other under all fuel scenarios
  - MBE4000 emits  $\sim <1/10^{\text{th}}$  of the average of C15 and ISM engines
- Carbonyls
  - C15 and ISM engines perform similarly to each other under all fuel scenarios
  - MBE4000 emits  $\sim <1/6^{\text{th}}$  of the average of C15 and ISM engines